Idaho National Engineering and Environmental Laboratory

Fundamental UNEX Chemistry

Project #81995

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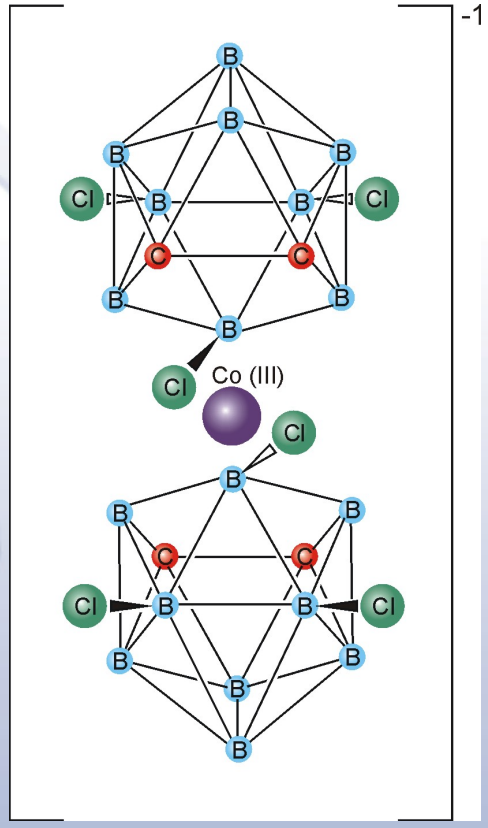
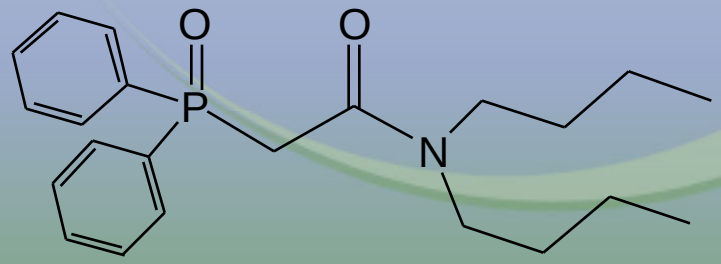
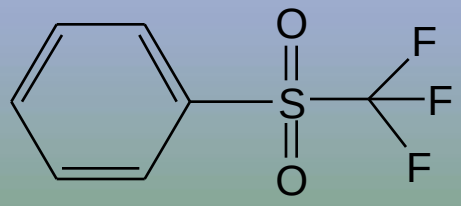
Background: The UNEX Solvent System

- *Chlorinated Cobalt Dicarbollide (CCD) for Cs extraction.*
- *Polyethylene glycol (PEG-400) for Sr extraction.*
- *Diphenyl-N,N'-di-n-butylcarbamoyl-methylphosphine oxide (CMPO) for actinide extraction.*
- *Current diluent is phenyltrifluoromethyl sulfone (FS-13).*



$HO(CH_2CH_2O)_{8\text{-}10}H$





RESEARCH OBJECTIVES

- ***UNEX Process indeed works, but how? - what fundamental chemistry occurs in the process?***

- ***The objective of this project is to define the underlying chemical phenomena (mechanisms) operative during the extraction process including-***
  - ***stoichiometry of extracted species***
  - ***effects of water, nitrate, and acid***
  - ***solvent effects***

Extraction in CCD Systems

$$[M^{n+}]_{aq} + n[H^{+}\cdot bH_2O]_{org} + n[CCD^{-}]_{org} \bullet$$

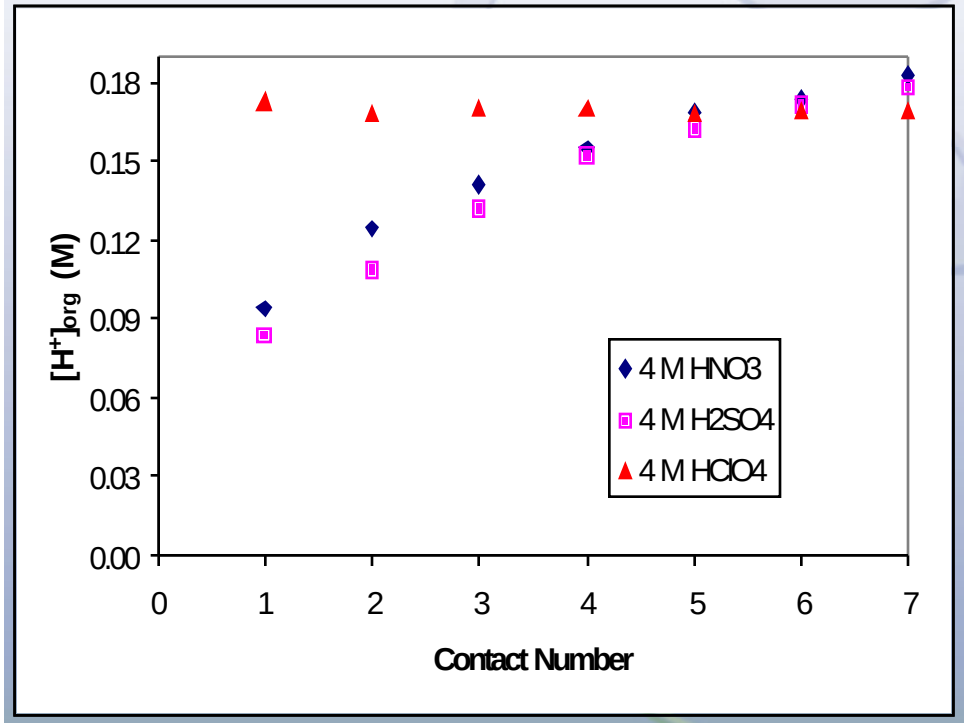
$$[M^{n+}]_{org} + n[H^{+}]_{aq} + bH_2O + n[CCD^{-}]_{org}$$

Acid (4 M)	*b*
$HClO_4$	5.3 ± 0.04
HNO_3	5.7 ± 0.06
H_2SO_4	5.4 ± 0.03
[a] Literature	5.5

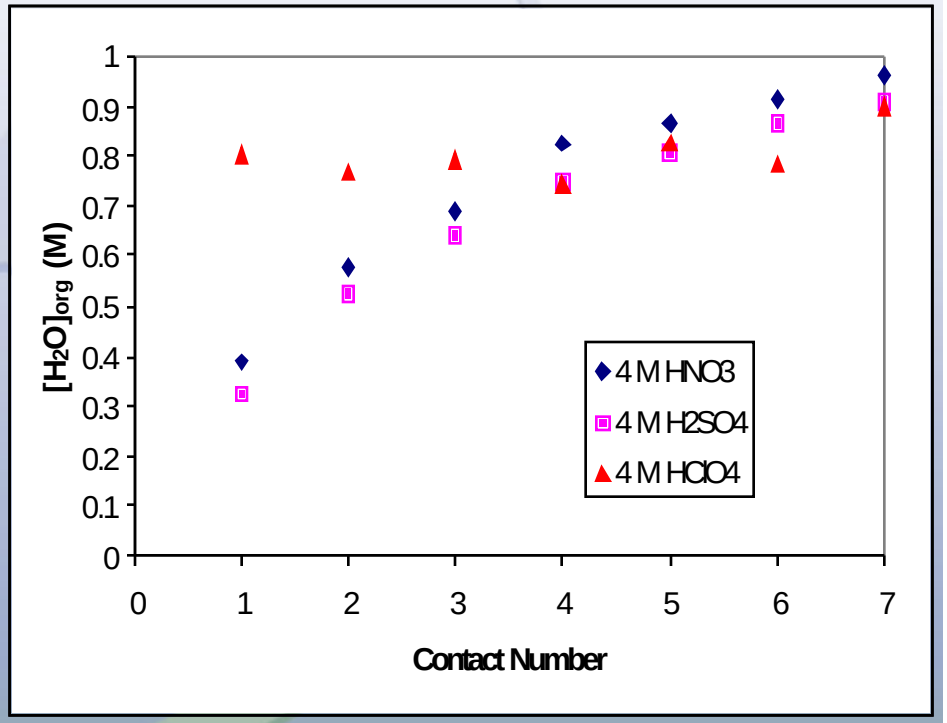
[a] Vanura, P.; Makrlik, E.; Rais, I.; Kyrs, M. *Coll. Czech. Chem. Commun*. **1982,** *Vol. 5 (47)*, 1444-1464

Cs Extraction in CCD Systems - Organic Phase Acid/Water Content

Initial Org. Phase: ~ 0.16 M CsCCD in FS-13



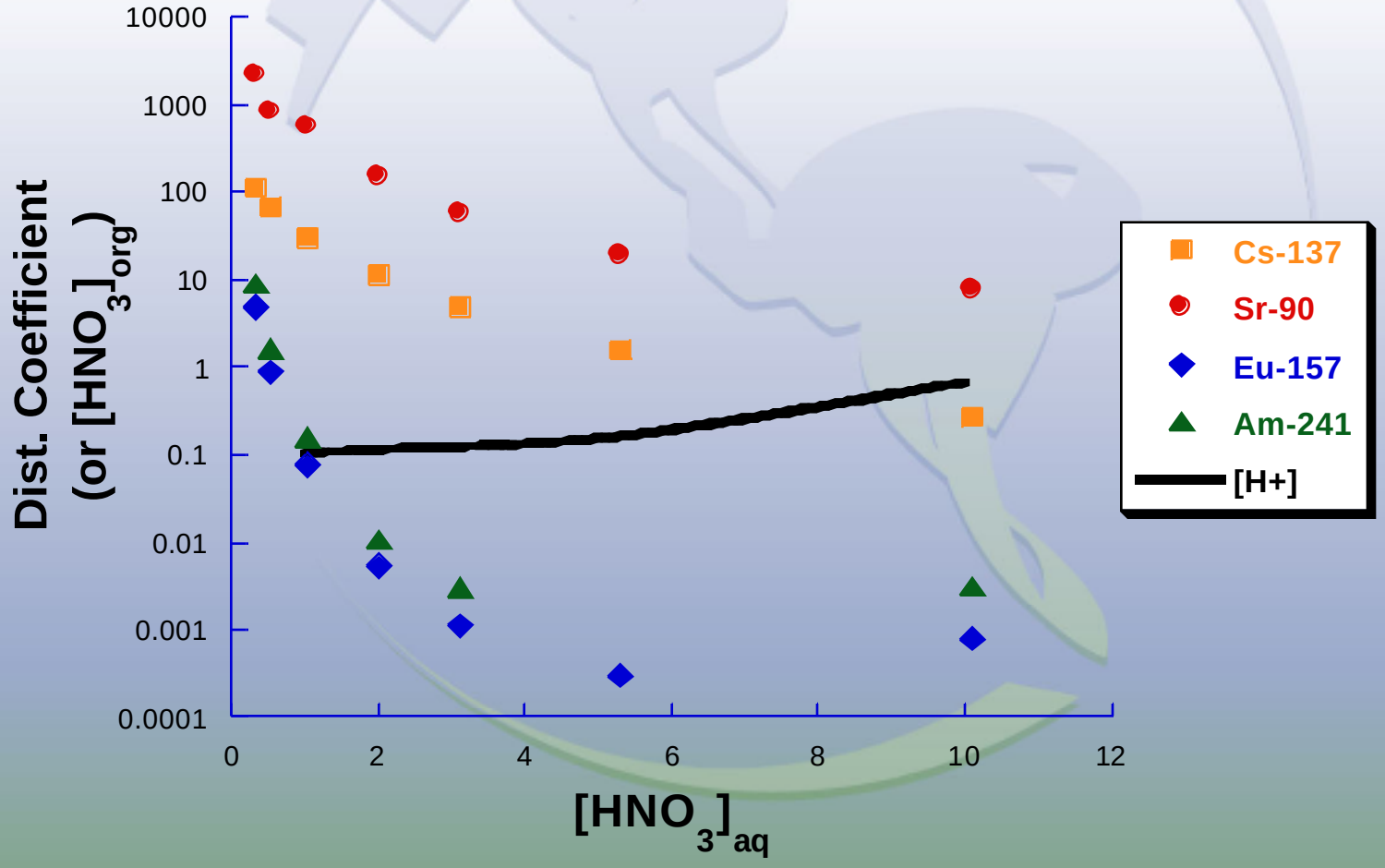
Acid concentration (Potentiometric Titration)

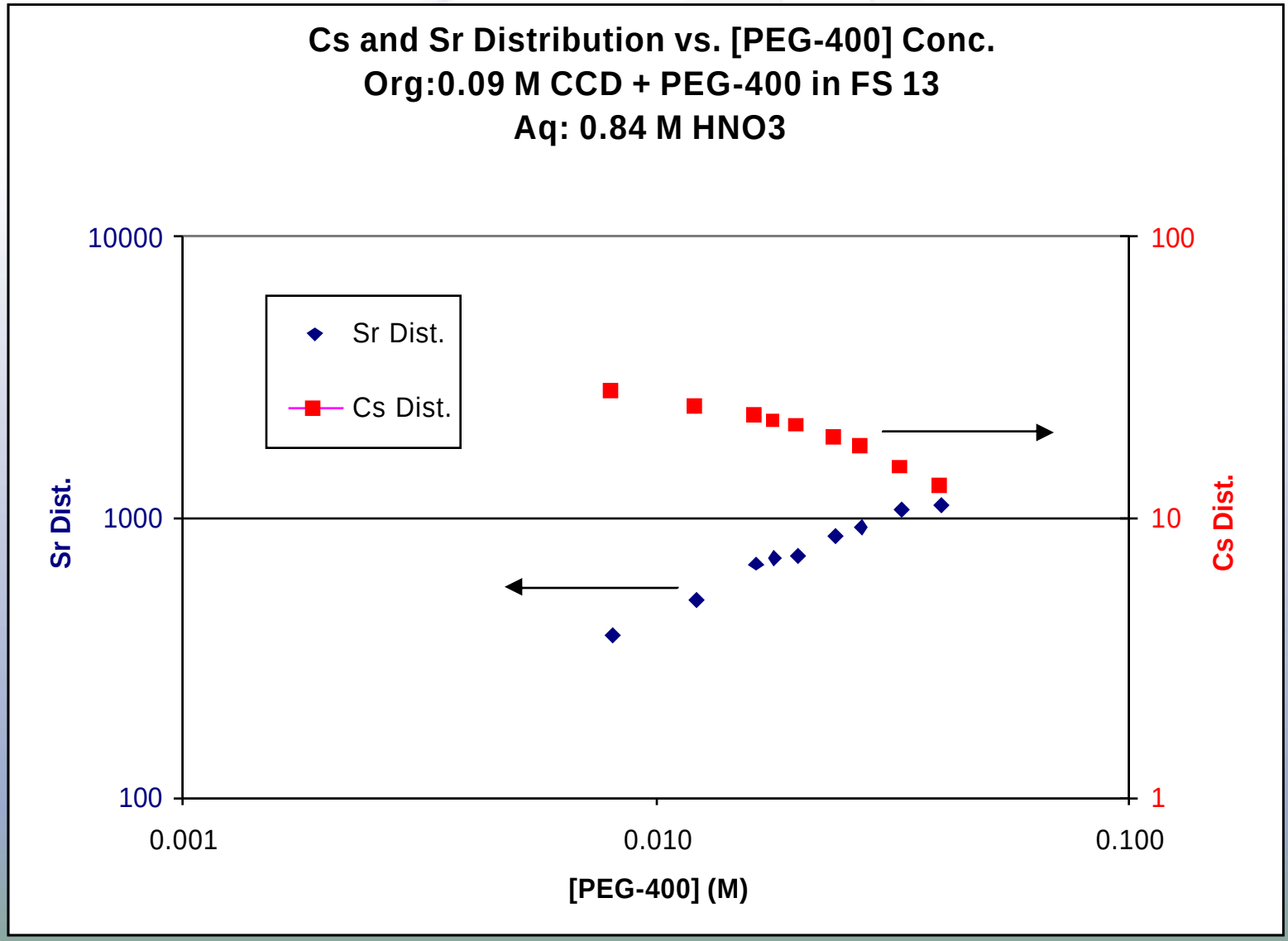


Water concentration (Karl Fischer Titration)

Extraction Dependency on Aqueous [HNO_3]

Organic Phase: 0.08 M CCD + 0.016 M PEG-400 in FS-13 (25 °C)




Cs and Sr Distribution vs. [PEG-400] Conc.
Org:0.09 M CCD + PEG-400 in FS 13
Aq: 0.84 M HNO3
10000
1000
100
100
10
1
Sr Dist.
Cs Dist.
Sr Dist.
Cs Dist.
0.001
0.010
0.100
[PEG-400] (M)

Organic Phase Strontium Complex

- ***IR spectroscopic studies of the organic phase:***
  - ***Sr^{+2} saturated solution of***

    0.05 M CCD in DCE (w/o PEG):

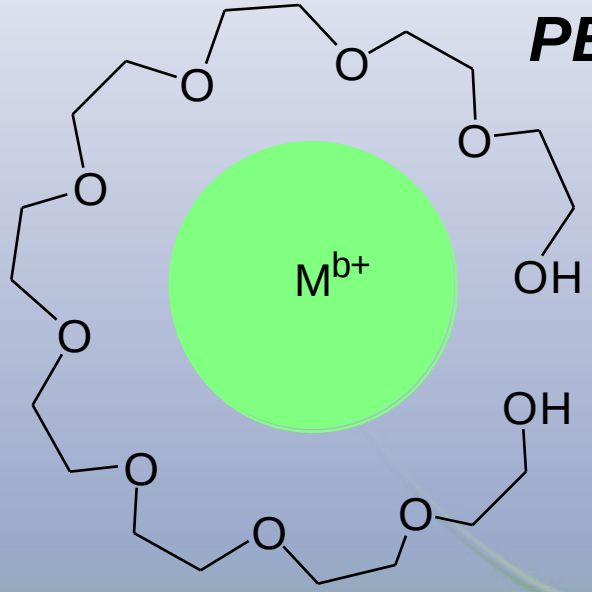
    $[Sr^{+2}\bullet 8H_2O]\ CCD^{-}_{2}$
  - ***Sr^{+2} saturated solution of***

    0.05 M CCD & 0.05 M PEG-400 in DCE:

    $[Sr^{+2}\bullet PEG]\ CCD^{-}_{2}$ 1:1 Sr:PEG Complex

Organic Phase Strontium Complex

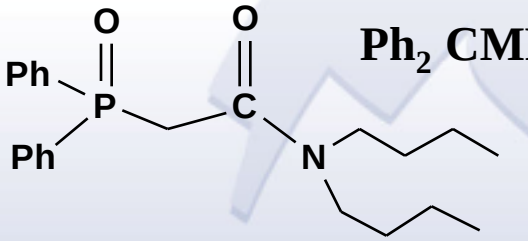
Ethereal oxygen's in PEG displace 8 H_2O molecules from 1st coordination sphere. Consistent with Sr^{+2} extraction data vs. PEG size:



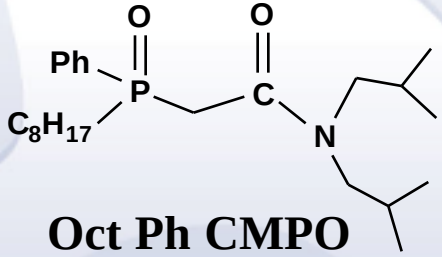
	Ave. n	D_{Sr}
PEG-300	6-7	4.0
PEG-400	8-10	4.1
PEG-1500	33-34	0.6

$HO(CH_2CH_2O)_nH$

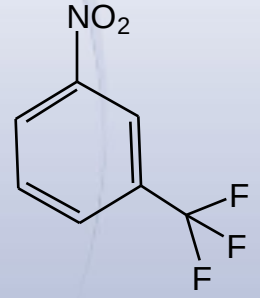
ACTINIDE EXTRACTION BY CMPO:



Ph_2 CMPO



Oct Ph CMPO



Distribution Data

Aq: 3M HNO_3 Org: 0.005 M CMPO in F-3

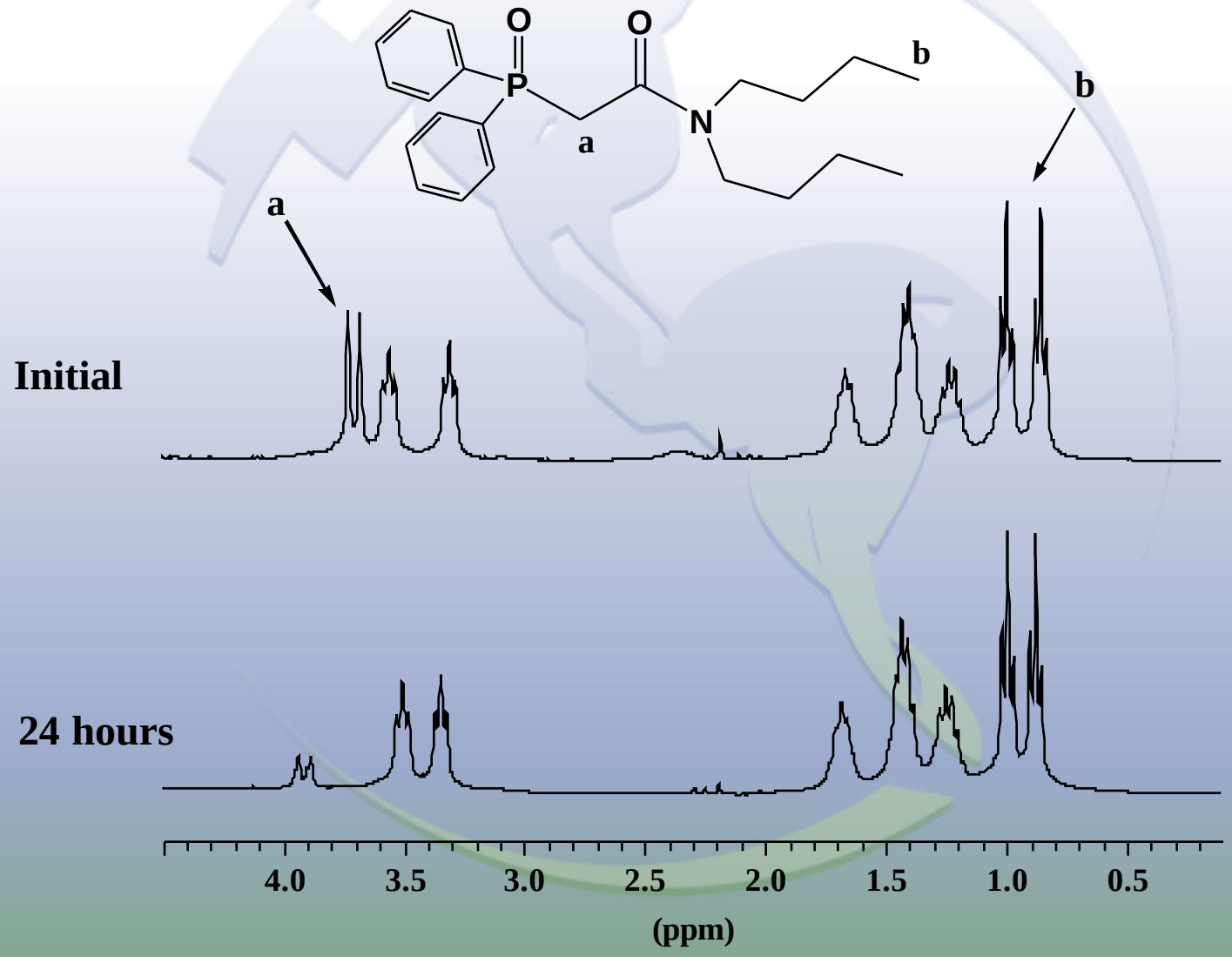
Extractant	D_{Am}	D_{Eu}	$K_{HNO3, Ex}$
Oct Ph CMPO	0.05	0.03	2.0 [a]
Ph_2 CMPO	0.45	0.30	0.76 [a]

[a] Data of Horowitz, et. al. 1986

H — D Exchange

- ***Exchange of protons for deuterium in the methylene bridge observed in NMR spectra of both CMPO compounds.***
- ***Exchange initiated using 3 M HNO_3, DNO_3, $HClO_4$, $DClO_4$, $LiNO_3$ + $La(NO_3)_3$, or $NaNO_3$ + $La(NO_3)_3$, each in D_2O.***
- ***Acidity of bridge protons indicative of compound basicity.***

H — D Exchange



D_{Am} vs. H-D Exchange Rate (•)

Extractant	D_{Am}	• (hrs)
Oct Ph CMPO	0.05	24
Ph_2 CMPO	0.45	6 - 7

SUMMARY

- ***In the HCCD/PEG-400 system, simultaneous Cs/Sr extraction can be represented by the following (simplified) reactions:***

$$[Cs^{+}]_{aq} + [HCCD]_{org} \bullet \quad [H^{+}]_{aq} + [CsCCD]_{org}$$

$$[Sr^{2+}]_{aq} + [PEG]_{org} + 2[HCCD]_{org} \bullet \quad 2[H^{+}]_{aq} + [Sr \cdot PEG \cdot CCD_{2}]_{org}$$

- ***H-D exchange in the methylene bridge of CMPO has been observed. Rate of exchange qualitatively interpreted to indicate bidentate coordination of hydrated proton with CMPO.***

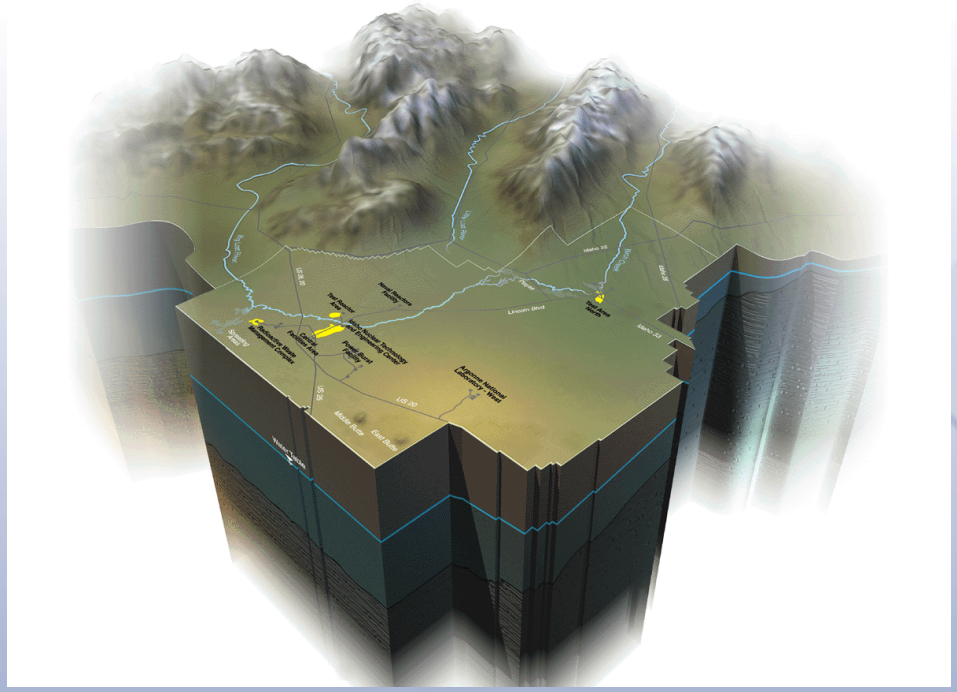
Research Highlights

- ***5 Journal Articles published/accepted/submitted thus far.***
  - ***2 drafted***
  - ***Several others planned***
- ***6 Technical presentations at National/International meetings***
- ***1 Graduate student supported***
- ***Cs/Sr Extraction results used to define solvent composition for spent nuclear fuel treatment in the DOE NE Advanced Fuel Cycle Initiative***

Future Research Direction

- ***Emphasis in FY-05 (final year of project) on further evaluation of actinide/lanthanide interactions with CMPO in the UNEX system:***
  - ***Non-synergistic (independent) of PEG?***
  - ***Anion stabilization (CCD^- vs. to NO_3^-)?***
- ***Verify of bidentate coordination of CMPO and hydrated H^+ in the organic phase.***
- ***Evaluation of organic phase structures via IR and NMR spectroscopic techniques.***

Acknowledgments



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